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CHEMICAL SPECTROSCOPY

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I. Introduction

The purpose of chemical spectroscopy with neutrons is to utilize the dependence of neutron scattering cross-sections on isotope and on momentum transfer (which probes the spatial extent of the excitation) to understand fundamental and applied aspects of the dynamics of molecules and fluids. Current interest is concerned with elucidating the relationship between dynamics and the potential governing molecular motions. Examples of such studies are the determination of force fields and of crystals fields responsible for physisorption, chemisorption, transport on surfaces, intercalation, and adsorption by catalytic materials such as zeolites.

Three unique properties of neutron scattering are of significance for this type of work: (1) the use of momentum transfers between 0.1 A^{-1} and 10 A^{-1} to define quantities such a) as the eigenvectors of molecular vibrations (independently of the eigenfrequencies which are obtainable from IR or Raman spectroscopy), b) the Elastic Incoherent Structure Factors (EISF) for molecular motion, and the characteristics of this motion such as rotational diffusion by small steps, jumps, or continuous reorientation, ion diffusion, and the scaling of molecular diffusional dynamics and validity of equations of motion for transport over atomic distances; (2) the very large incoherent scattering cross-section of hydrogen and the contrast available because of the neutron scattering operator and through isotopic substitution which allows for the separation of scattering, for instance from a substrate and adsorbate, into the two components and identification of cross terms between them; (3) the very high energy

resolution of neutron scattering at low energy transfers, which has revealed, e.g., tunneling phenomena that are a key to determining self-consistent potentials for the crystal fields mentioned above. One particularly important application of higher intensity neutron sources would be the extension of the high resolution capability to higher energy transfers.

In the following discussion we have divided the area of chemical spectroscopy into three energy ranges, which at present sources are principally covered by three classes of spectrometers, as follow: (1) Vibrational spectroscopy, 25 - 500 meV, for which much of the work is done on Be-filter analyzer instruments; (2) Low energy spectroscopy, < 25 meV, for which the prototypical spectrometers are IN4 and IN6 at the ILL; and (3) High resolution spectroscopy, < 1 meV, which typically is performed on the backscattering spectrometers IN13, IN10, or the TOF spectrometer IN5.

II. Vibrational Spectroscopy

We have identified three major areas for significant improvements on the current work in neutron vibrational spectroscopy that wou<. i uniquely be provided by an advanced neutron source. These are the measurement of he Q-dependence of the vibrational spectra, higher energy resolution as well as an extension of the Q-range to much lower values at high energy trans-fers, and the provision of higher sensitivities. We will now discuss representative examples in each of these categories.

(1) High energy resolution studies which include Q-dependence. Much of the current work involving inelastic incoherent neutron scattering (IINS) vibrational spectroscopy suffers from the fact that data are coi-lected at high momentum transfers (as much as 15 A^{-1}). The reason for this is that at many present sources high count rate analyzers must be used to collect this data. These are usually low energy band pass filters for which $|k_f|$ is small compared with $|k_i|$, such that the momentum transfer increases with incident energy. As a result the spectra at high energy transfers are often contaminated with combination and overtone bands and therefore single phonon peaks and their intensities are often difficult to
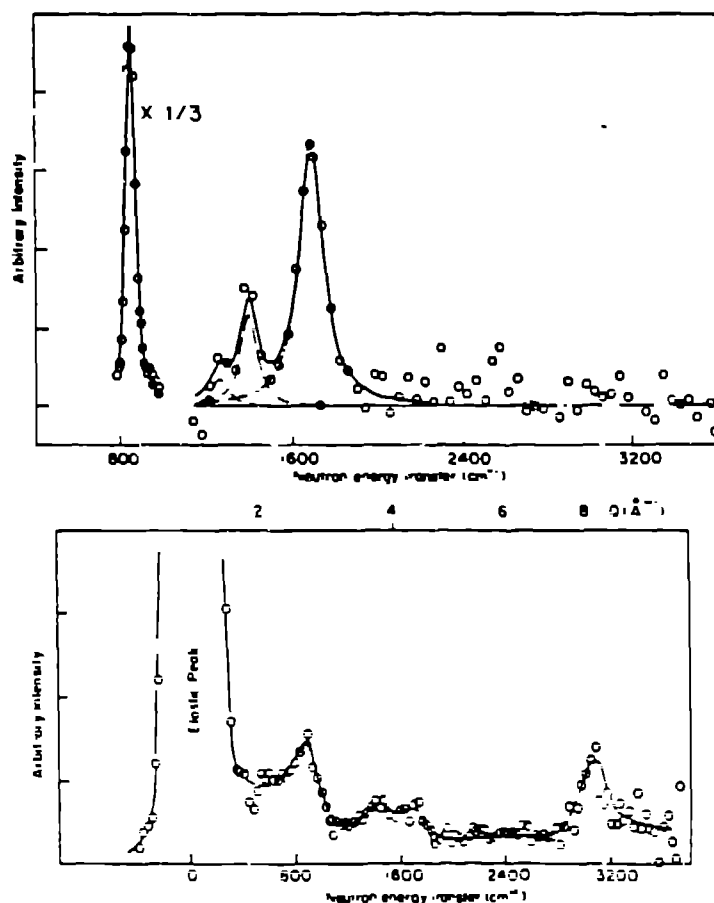
Figure 1: The IINS spectra of $HCCo_3(CO)_9$ obtained on the FDS at Los Alamos (top, $T = 15K$) and the IRS at Harwell (bottom, $T = 90K$). Note the lack of signal in the $C-H$ stretching region in the FDS spectrum ($Q \sim 13 \text{ A}^{-1}$ at 3000 cm^{-1}).

obtain. There is good reason to believe [1]. that many of the published spectra of C-H stretching modes by IINS are doubtful because of this contamination [Fig. 1]. The importance of extracting accurate one-phonon intensities from IINS spectra lies in the unique property of neutron scattering. namely that intensities can be calculated exactly and can be utilized for making mode assignments   This procedure then leads to the deduction of force fields. which for instance are needed as input parameters to the calculations of IR intensities. a subject of great importance in spectroscopy

In order to obtain more accurate one-phonon intensities vibrational spectra must be taken as a function of momentum transfer and with better energy resolution than is currently possible   This will minimize multi-phonon contributions and allow distinction between overtones and single phonon excitations.   Such measurements would require. for example. a resolution of at least 2 meV at an energy transfer of 200 meV and a minimum attainable momentum transfer of approximately 2 A^{-1}.   The instrument of

choice for this type of measurement would be a chopper spectrometer at an advanced pulsed neutron source utilizing short pulse widths with incident energies between .5 and 2 eV and a flux at the sample of at least 10^5 n/cm^2 sec.

The ability to measure vibrational spectra with much higher resolution is of particular importance for complex molecules, which typically also have the most uncertainties in the assignments of vibrational frequencies. Even prototypical hydrogen-bonded systems (which have been studied extensively by many techniques) are often poorly understood. One such example are the Bifluoride and related systems, where a recent measurement with higher resolution revealed an unexpected splitting in the intense bending mode [2]. This work needs to be repeated with a highly dilute (factor of 100) system to resolve the question on the origin of this splitting. This is just one of many cases of even relatively simple compounds where high resolution is essential for mapping out details of the potential surfaces in question. Furthermore, it would be of great interest to use a single crystal in this case to orient the potential with respect to the incident neutron beam. This would provide additional information on the anisotropy of the potential. It may be desirable to also have a spectrometer with a large focusing crystal monochromator for this type of measurement.

Considerable effort has gone into computing and mapping out of potential surfaces of hydrogen trapped in metals which is an essential step towards understanding the bonding and diffusion processes in these important materials. Most of the experimental work that included the observation of more than the lowest bound states has been limited either to concentrated samples or to measurements without Q-dependence. The potential of dilute H in bcc metals is known to be very anharmonic and the observed transition lines have as yet unexplained line widths. A determination of the full $S(Q,\omega)$ would -- in conjunction with theoretical modelling -- provide detailed information on the proton wave function and the potential. In addition, the transition to recoil scattering of the proton can be studied if a high enough incident energy is available. The range of $S(Q,\omega)$ that would be required for this class of experiments is roughly $\omega < 1000$ meV, and 2 A$^{-1} < Q < 25$ A^{-1}.

There are numerous other cases where present source intensities do not allow resolution improvements necessary to do the experiments. Recent theoretical work by M. Warner and collaborators [3] has, for instance, pointed out the possibility of studying the coupling between internal and

external modes by measuring the fine structure of the vibrational transitions. Other examples include the exciting possibility of distinguishing either molecules adsorbed on different sites of a catalyst or different molecular species resulting from a catalytic reaction by differences in their respective vibrational spectra, or an accurate determination of the crystal field splittings, e.g., of the rotational transition lines of H_2 in graphite intercalation compounds [4]. The intercalated graphite substrate imposes a relatively weak crystal field on the rotations of the hydrogen molecule which split the transition levels [Fig. 2] by 1-2 meV at energy transfers going above 200 meV. This is a dilute system which requires high energy resolution and low Q to obtain detailed information on the interaction of H_2 with the substrate. Even with the next generation source the energy resolution is such that the data are not likely to be fully resolved. Some curve fitting is thus likely to be necessary. This problem
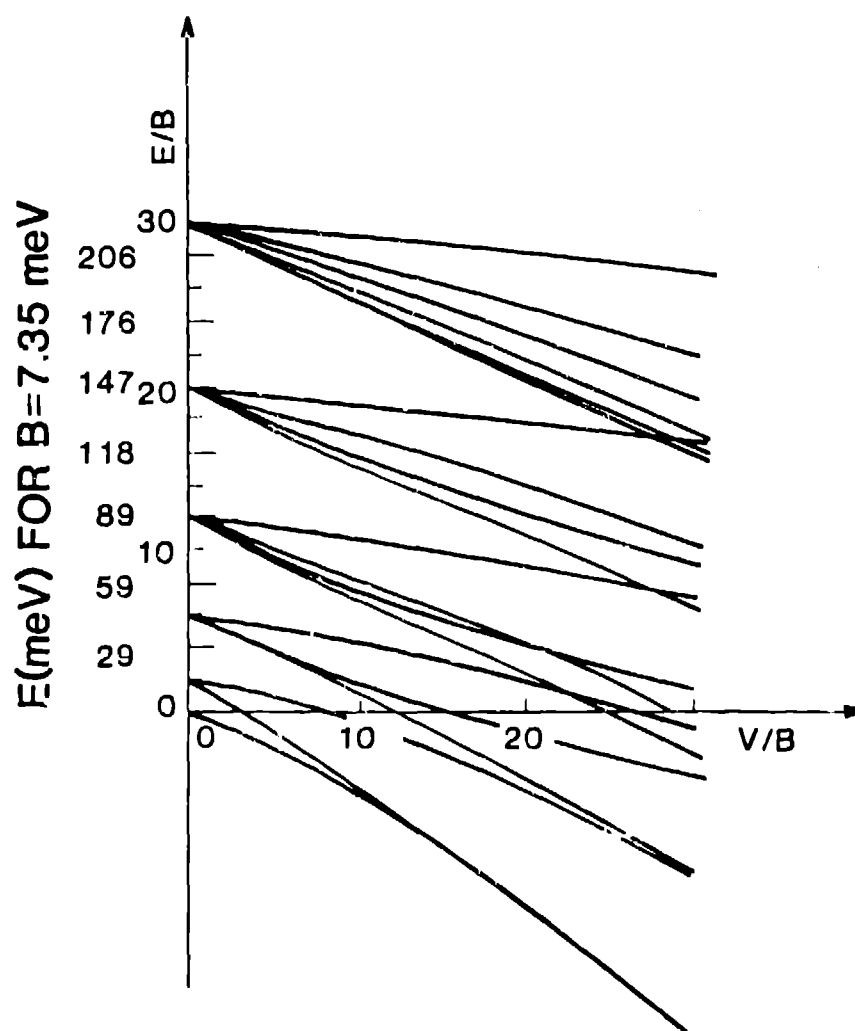

Figure 2: Calculated crystal field levels of H_2 in a crystal field. Note that for small values of V high resolution is required at large energy transfers to resolve the levels.

is made even more severe because the required optimum Q values (~ 1.5 A^{-1})
impose such a high E_1 that ΔE becomes unacceptably large.

A large number of important spectroscopic experiments need to be done
on loosely bound molecules. This has in general not been possible because
of the requirement to keep Q well below 3 A^{-1} at as high an energy transfer
as possible even if modest energy resolution is acceptable. This would
allow the study of physisorbed molecules or molecules in aqueous as well as
nonaqueous solution. This has been shown in at least two recent examples
where the normal modes of species in concentrated solution have been ob-
served. The first of these [5] involves the observation of the torsional
modes of the $N(CH_3)_4^+$ ion in D_2O at energies less than 40 meV, while in the
second experiment detailed data were obtained [6] up to 450 meV for
chloroform ($CHCl_3$) in liquid sulfur dioxide [Fig. 3]. This demonstrated
ability to study species in various types of solution is chemically very
important. The method can, however, only be more fully exploited if dilute
solutions can be examined and data collected over a wide range of Q,
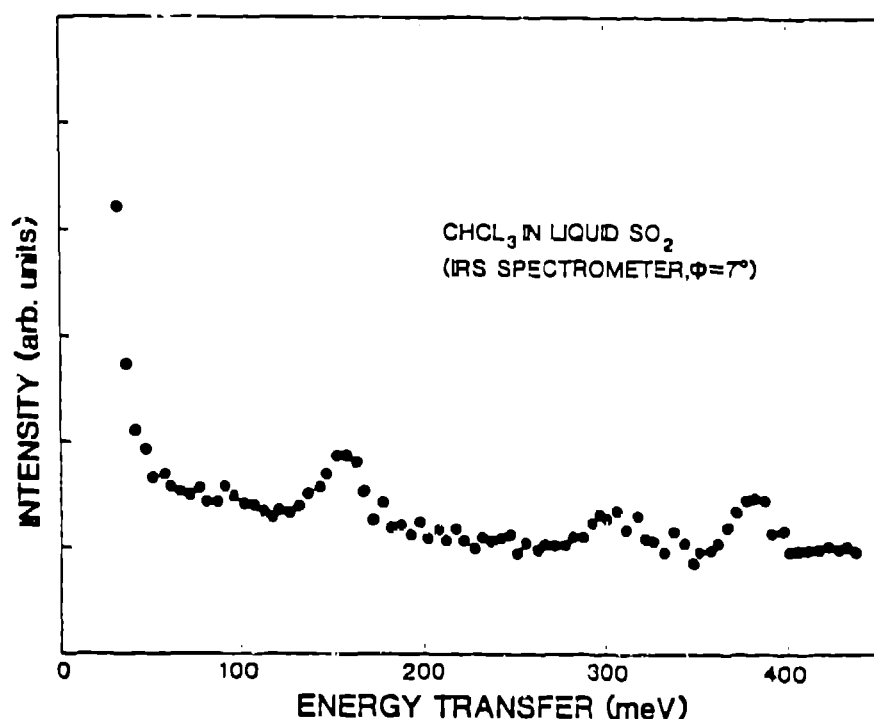including low Q (< 6 A^{-1} at 400 meV).

Figure 3: IINS spectrum of $CHCl_3$ in liquid SO_2

(2) Medium resolution vibrational spectroscopy. There exists a
range of problems for which even at an advanced source the intensity will
not be sufficient for Q dependent and high energy resolution measurements
to be feasible. Despite this the reasons for doing this type of experiment

are essentially identical to those outlined in the previous section.

The factors which contribute to the requirement for such a high sensitivity spectrometer may be listed in terms of the approximate increase in flux at the sample (incl. energy analysis) that is necessary over current spectrometers as follows:

-- effect of dilution: 10-100
-- smaller cross section samples: 1- 40
-- differential spectroscopy: 10

Thus the combined need for intensity increases ranges from a factor of 100 to 40,000! We will now describe some representative examples for each of these categories.

(A) Differential Spectroscopy. Excellent statistics are required if differences at the level of less than a percent are to be observed between samples of very similar cross-sections. These difficulties are aggravated for difference studies on dilute media. Examples include:

(a) Molecules on the surface of colloidal particles

(b) Species adsorbed on catalysts, particular supported catalysts since in these cases the surface areas and adsorption capacities are extremely low; this type of work should also be extended to include adsorbates with low cross-section, i.e., molecules not containing hydrogen.

(c) Molecules intercalated between graphite layers. A great deal of pioneering work has been performed on the dynamics of small molecules on high surface area (10 m^2/gm) graphite substrates. At energy transfers below 50 meV, for example, the vibrational density of states of adsorbed CH_4 shows peaks
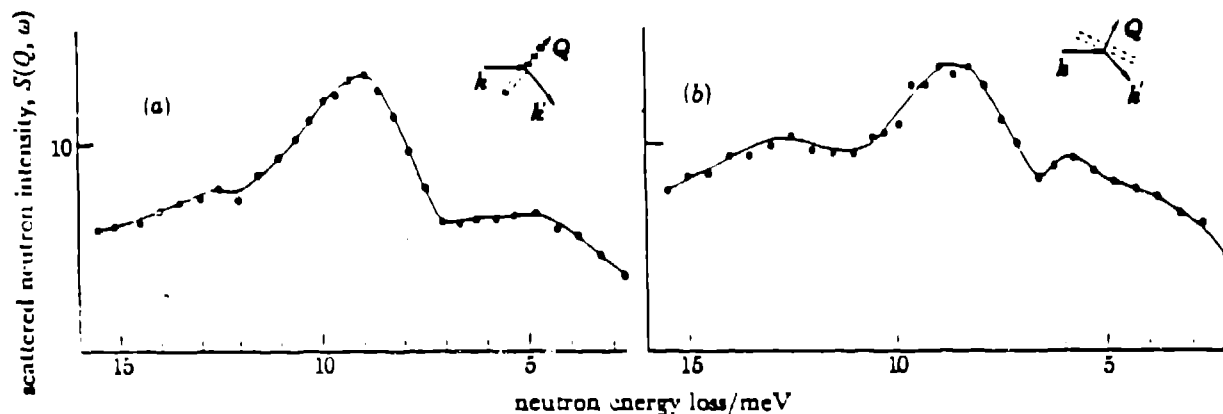

Figure 4: Vibrational spectra of 0.7 monolayers of methane adsorbed on exfoliated graphite, T ~ 10K, with Q parallel (a) and perpendicular (b) to the surface (Ref. 7).

[7] resulting from motion perpendicular and parallel to the surface as well as librational excitations in the crystal field that the surface provides [Fig. 4]. This type of measurement can be done with an energy resolution of ~ 1-3 meV, i.e., rather better than is possible with the best alternative techniques, e.g., electron energy loss spectroscopy. An increase in neutron source flux would therefore allow spectra of this quality to be taken -- even with current spectrometers -- on a much wider range of substrates whose specific surface area is much less than that of graphite.

(d) Modulation experiments. An example of this category would be the study of changes that take place in an electrode surface layer as a function of changes in the applied potential.

(e) Isotopic substitution. The most common case is the selective replacement of hydrogen with deuterium because of their large difference in cross-section. This is an extremely powerful aid in the assignment of vibrational spectra. Higher neutron source fluxes would allow other substitutions, such as $^{14}N/^{15}N$ or $^{35}Cl/^{37}Cl$. For example, it would be desirable to study the DF_2^- ion at ca 1% incorporation in an alkali halide lattice in order to help answer questions (see Section II.1) on this basic hydrogen bonded system. The bifluoride cross-section at this dilution would be reduced by a factor of 1000 over that of the parent $NaHF_2$.

(B) Time-dependent processes. For compatibility with other techniques it is desirable to obtain spectra in very short times. By reasonable extrapolation of current spectrometer performance it can be shown that in favorable cases a vibrational spectrum can be taken in about one second at an advanced neutron source. This makes it feasible to study a range of relatively slow, but nevertheless important chemical phenomena. These include, for example:

(a) Reactions in alumino silicate frameworks, e.g., the isomerization of cyclopropane to propene, described below;

(b) The competitive adsorption of reactants and products or the changes which occur during the displacement of one species by another;

(c) Changes which accompany intercalation and adsorption.

During the isomerization of cyclopropane over some zeolites (e.g., ZnNaA)

It has been shown [8] that the production of propene can be followed over a time period from one second to one hour. During this period the relative intensities and frequencies of the IR bands from the adsorbed reactant change significantly. Since the zeolite is strongly absorbing below 150 meV, several of the internal modes cannot be observed using IR. Neutron scattering studies would make it possible to supply the missing data as well as to give information on the important modes of the zeolite/ C_3H_6 system, i.e., those which directly reflect the strength and nature of the interaction of the adsorbed molecule with the surface.

For the above types of measurements a spectrometer with very high sensitivity is required. This suggests an instrument which integrates counts over a large solid angle (no Q resolution), an advanced analog to such instruments as the FDS (Los Alamos), CAS (Argonne), the INIB (ILL), or the BT-4 (TRASH) at NBS. It is essential, however, that the energy resolution be superior to that available at this time, so that reasonably well resolved spectra can be obtained for mode assignments and intensity calculation. A factor of two improvement in resolution could then be combined with the other factors mentioned at the beginning of Section II.2 to imply a required intensity increase of a factor 400 to more than 100,000 over current instruments at medium flux sources for this type of spectroscopy.

III. Low Energy Spectroscopy (E ≤ 25 meV)

The future needs for chemical applications in this energy regime lie in at least three different areas, two of which are analgous to the case of vibrational spectroscopy, namely better energy resolution on the one hand, or higher sensitivity on the other. A third, potentially very important class of experiments would utilize polarization analysis.

(1) High energy resolution studies. The first class of experiments requires the attainment of even better energy resolution (10-20 ueV) in order to allow for example the probing of molecular motions which more closely overlap the NMR range. This must be achieved with the same high sensitivity as discussed below and over a Q range extending to 2.5 A^{-1} in order to unravel the geometry of long-range diffusive and rotational motions. A large number of systems involving isolated or weakly interacting molecular groups could be investigated with such a measurement capability. For example [9], existing facilities at the ILL and at NDS have been used to establish for the first time the detailed potential hindering the rotation of the methyl group in the solid phase of nitromethane [Figs.
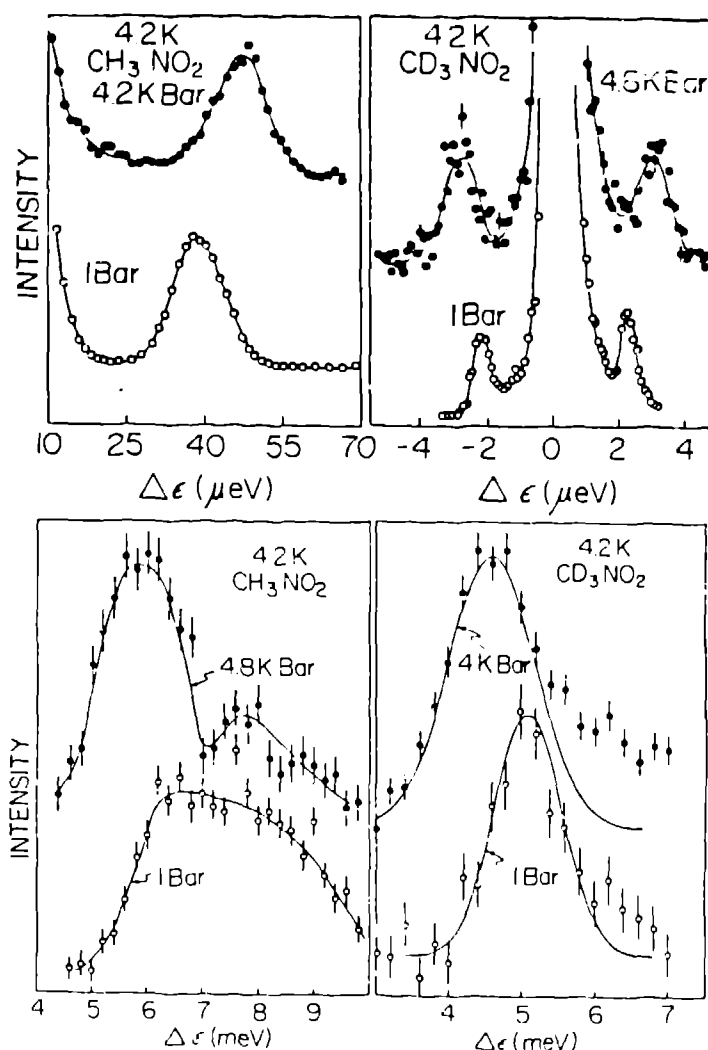
Figure 5: Inelastic neutron scattering spectra of CH_3NO_2 at 4.2K and pressures of 1 bar and 4.8 kbar. The top part shows the pressure dependence of the ground state tunnel splitting, the bottom part that of the first excited torsional level.

5 and 6]. However, it is not at present possible to extend these measurements to dilute molecular systems.

The ability to probe molecular motion and processes in this range of Q and energy transfer will open up important new research opportunities in many chemical systems, including transport mechanisms in glassy or crystalline superionic conductors, chemical exchange reactions, solvent exchange in colloidal suspensions, and the dynamics of coordinated molecules around complexes in ionic solutions, as well as on chemisorbed or intercalated molecular species. Such instruments would have a great impact on similar studies which are at the interface between physics and chemistry. A recent example is the unique study of hydrogen tunneling around chemical impurities in superconducting metals at extreme dilution. The effects of a
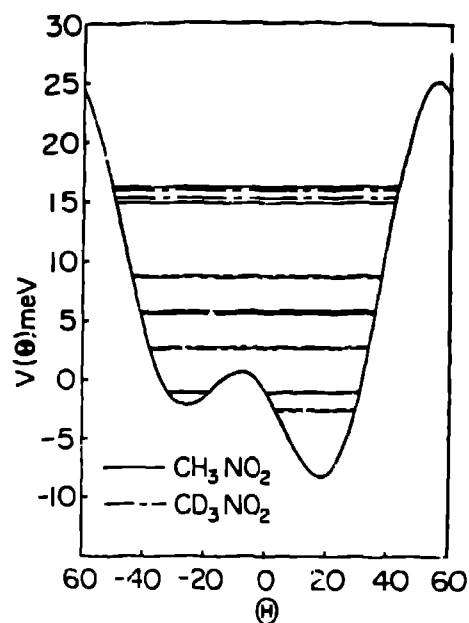
Figure 6: The rotational potential of nitromethane as a function of methyl group rotation with parameters corresponding to 1 bar.
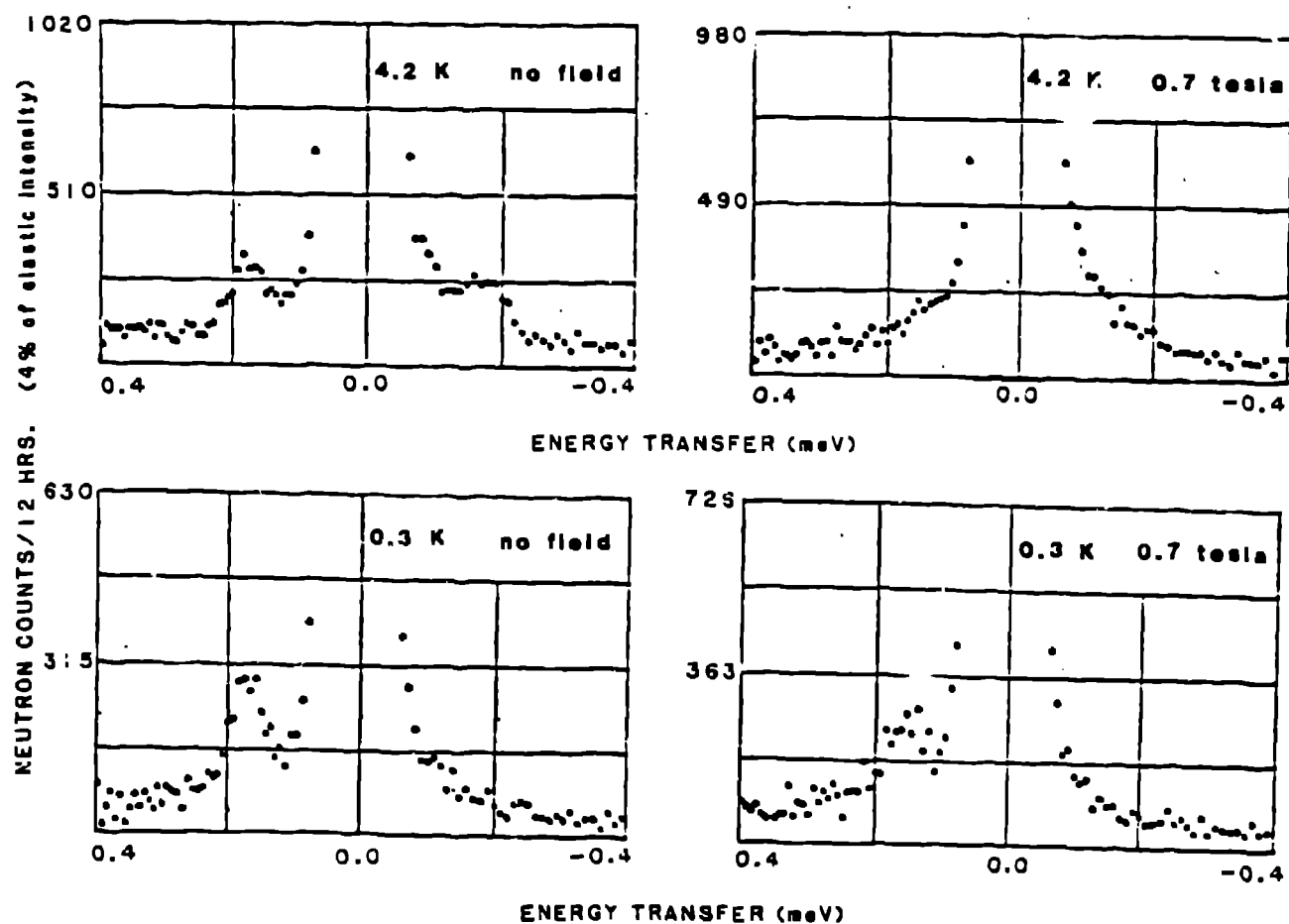

Figure 7: Tunneling states of H trapped at oxygen impurities in Nb. The sample was 50 g of $NbO_x II_y$ with x = y = 0.00015.

magnetic field on these tunneling states in studies of oxygen traps in Nb
on the IN6 spectrometer at the ILL are shown in Fig. 7.

(2) High sensitivity studies. For a second class of problems it would
be desirable to achieve still higher sensitivity using neutron beams with
incident energies of 10-20 meV and Q's up to 5 A^{-1} at a resolution of
about 0.1 meV with a large solid angle of detection. This capability is
essential to allow, e.g., the measurement of hindered rotational or tor-
sional levels in dilute molecular species bound in chemical adsorbents,
catalysts or in layered or intercalated materials, as well as for the study
of the form factor or diffusion paths of species undergoing reorientation
or diffusion. Such information is the key to a fundame tal understanding
of bonding potentials and local transport of chemical fragments or species
in dilute media, and to probe the effect of intermolecular interactions on
these potentials. These interactions are often a dominant factor in deter-
mining reactivity and exchange in chemical systems.
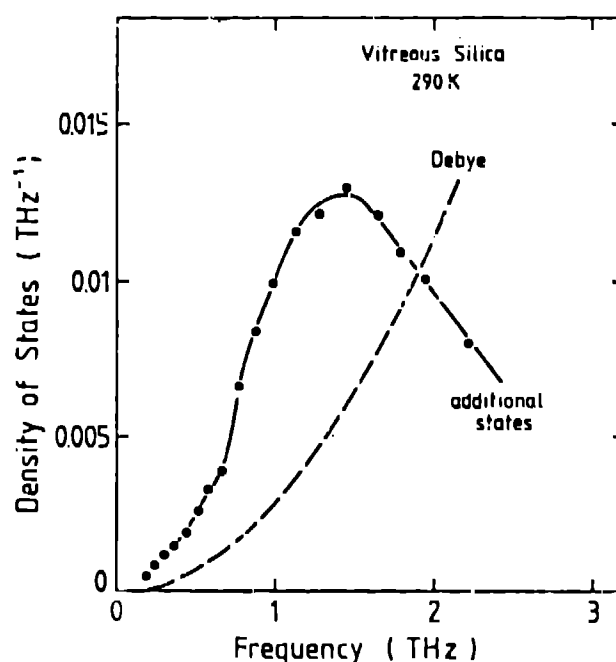

Figure 8: Density of states of additional low frequency modes in vitreous
silica compared to the Debye density of states (Ref. 10).

Such an instrument would also permit a wide range of other applica-
tions, such as studies [10] of low energy excitations in disordered
materials [Fig. 8] which are critical to understanding the low temperature
specific heat anomalies in these systems (fractal behavior, two-level
systems, etc.). The search for low frequency motions of macromolecules,
which are postulated to be a key to the biological activity of enzymes, is

another area that requires extremely high sensitivity since those typically are difference experiments on very small samples looking for relative changes of presumably less than 1%. Neutrons have a unique role to play in those areas. and the increased flux required to do this experiments (at least 10^5 n/cm^2 -sec on the sample including energy analysis) is crucial.

(3) Polarization analysis. The quasielastic region, however, contains not only incoherent scattering from the dynamical process of interest but also coherent Bragg scattering. especially when the shorter incident wave lengths are used. which is particularly severe in the case of adsorbed molecules. Measurements of the Q dependence of intensities of the quasielastic scattering in these cases have therefore proved nearly impossible. A possible answer to this interference is the use of polarization analysis. Preliminary considerations show this to be technically feasible with the higher flux of an advanced neutron source. The idea was demonstrated fifteen years ago by Moon, Riste. and Koehler. but has not been extensively applied for lack of efficient. cheap. and simple neutron polarizers and analyzers

The method depends on the fact that the neutron nuclear interaction is spin-dependent of the form

$$V(r) \propto b\underline{S} \cdot \underline{I} \; \delta(\vec{R} - \vec{r}_j)$$

where S and I are the neutron and nuclear spin angular momenta. respectively The angular momentum operator can be expanded into $S_z I_z$. $S_+ I_-$. and $S_- I_+$. where the first term is associated with coherent. non spin-flip scattering and the other two with incoherent scattering processes. Thus for an incident polarized beam an analyzer could select that part of the scattering which has conserved spin angular momentum and is coherent. In the example of methane chemisorbed on graphite this would contain the Bragg scattering of the substrate (I = 0 for ^{12}C) and the coherent part of the methane structure factor. The incoherent part coming from translational diffusion. for example. would appear in the spin flip cross section.

The experimental possibility of such a separation has recently been demonstrated (with marginal statistics) on the new D7 instrument at the ILL by Prandl and collaborators in a study of the reorientational motions of C_2Cl_6 in its plastic crystalline phase [11]. Much higher intensity is clearly required here to perform such measurements on a more routine basis.

Many chemical problems would benefit from the installation of polarization analysis capability in the millivolt to microvolt energy transfer

regimes. Among these are: rotational diffusion processes in plastic and liquid crystals; oscillations and diffusion of physisorbed and chemisorbed molecules; measurements of the density of states in glasses and polymers at low energy transfers; solvent and solute motions in ionic and other solutions.

IV. Very High Resolution Spectroscopy

When a rotating molecule, such as one physisorbed on graphite, is cooled down, the rotational diffuse motions probed in the lower energy resolution measurements mentioned above slow down as jumps over barriers provided by the surface potential become less probable. For molecules with small moments of inertia (e.g., H_2, CH_4, etc.) rotational tunneling through
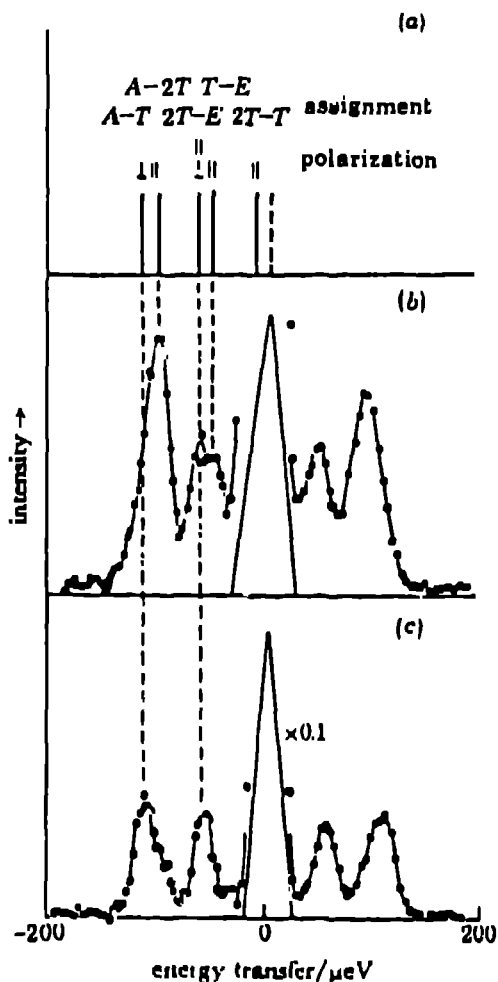

Figure 9: Rotational tunneling spectra (T = 4K) of 0.7 monolayers of methane adsorbed on exfoliated graphite. (a) Assignments and polarizations of the transitions; (b) Q parallel to the surface; (c) Q perpendicular to the surface.

a barrier may then be observed at low temperatures as an inelastic fine structure near E = 0 [12]. The study of tunneling spectra in molecular crystals is now well established and has also been utilized for both adsorbed H_2 and CH_4 [Fig. 9]. Complete interpretation of the positions intensities as well as polarization vectors leads to unique and extremely detailed information on the crystal field at the site of the tunneling molecule [13]. The application of these methods to a wide variety of molecules in dilute systems or adsorbed on a range of substrates could follow from the availability of higher intensity sources and neutron polarization analysis as discussed above (Section III.3). Other extensive areas of great importance in chemistry that would become accessible to a high resolution (~ 1-10 ueV for 0.3 ueV < ΔE < 5 meV) instrument with a Q range up to 2.5 A^{-1} are those where kinetic or exchange phenomena are involved. These include, for example:

(a) Exchange processes -- Between sites in solids

-- Between ions and solvents in solution (coordination spheres)

-- Around the surface of colloidal and polyelectrolyte particles

(b) Diffusion -- In molecular liquids

-- In superionic crystals

-- Of hydrogen in metals

Such a spectrometer is also required to extend the current work on the dynamics of macromolecules. Some of the above topics are also covered in more detail by the report of the subcommittee on Ultra High Resolution Studies.

V. Concluding Remarks

It should be apparent from the above discussion that the scientific opportunities in the area of chemical spectroscopy at a high intensity neutron source are enormous. Furthermore, we have identified several areas (such as time-dependent measurements) which are threshold experiments for a factor of ten increase in source flux and would not be possible by parallel improvements in instrumentation alone.

We have not considered questions on the types of spectrometers or pulsed vs. steady state neutron source in any detail. Available calculations [14] suggest that with one exception the experiments described in the body of this report could be equally well (to within factors of two or so)

be performed on appropriate pulsed source or reactor instruments. The exception to this are experiments requiring high energy transfers <u>with</u> a wide range of Q (Section II.1), which can only be done on a "true" (i.e., short pulse) pulsed neutron source because of the very high incident energies that are necessary.

Most of the examples identified as "high sensitivity" studies would require a flux on the sample of at least $10^5 n/cm^2$ .sec (including energy analysis after the sample in the case of inverted geometry spectrometers). We have therefore included [Fig. 10] some rough calculation of what resolution could be achieved at a 10^{17} peak flux pulsed source with a chopper spectrometer given the above requirement for flux on the sample under the condition $E_f = 1/2$ E_i. This figure shows that most of the resolution/flux requirements noted in our discussions could be met at an advanced neutron
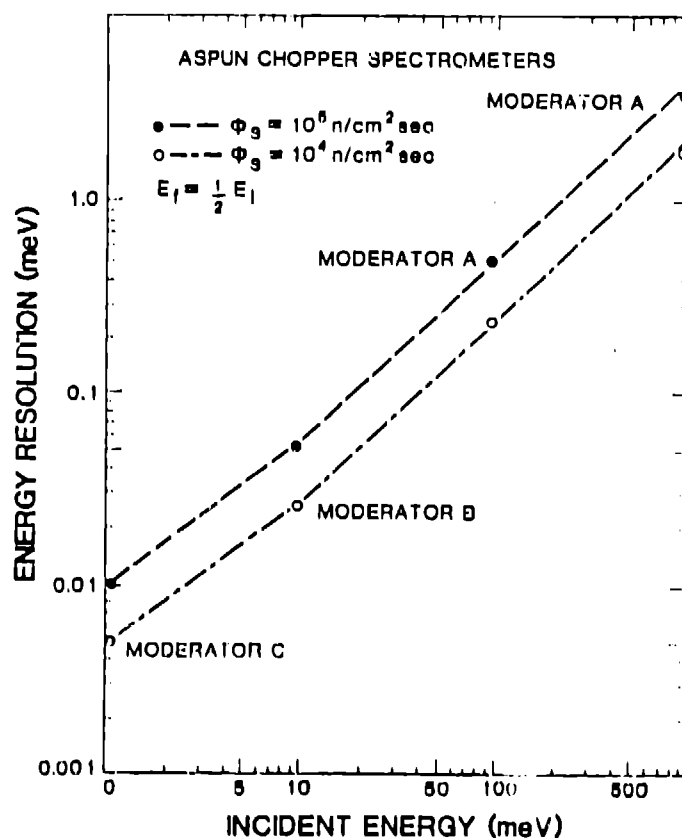

Figure 10: Calculated time-averaged neutron flux on the sample for chopper spectrometers at an advanced pulsed neutron source (peak flux 10^{17} n/cm^2 sec) for a given energy resolution and incident neutron energy under the condition $E_f = 0.5$ E.

source. It should also be pointed out, however, that this figure does not address the question of Q-resolution nor does it include polarization analysis.

We can summarize the minimum spectrometer needs at an advanced neutron source for chemical spectroscopy as follows:

I. <u>Vibrational Spectroscopy</u> (25 meV < E < 500 meV)\
   a) High resolution/Wide Q-range: $\Delta E \sim 1$ meV, $1\ A^{-1} < Q < 10\ A^{-1}$
   b) High sensitivity: $\Delta E \sim 2-3$ meV

II. <u>Low Energy Spectroscopy</u> (E < 25 meV)
   a) High resolution: $0.01 < \Delta E < 0.3$ meV

   b) High sensitivity: $\Delta E < .5$ meV $Q \lesssim 5\ A^{-1}$;

III. <u>Ultra-high resolution spectroscopy</u> ($E \lesssim 2$ meV)
   $0.001 < \Delta E < 0.002$ meV, $Q \lesssim 2.5\ A^{-1}$ incl. polarization analysis

It may, of course, be desirable to cover each of these five basic instrumental ranges with more than one, better optimized spectrometer.

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